PROCESS AND APPARATUS FOR LARGE-SCALE MANUFACTURING OF BULK MONOCRYSTALLINE GALLIUM-CONTAINING NITRIDE

CROSS-REFERENCES TO RELATED APPLICATIONS

This application is a continuation application of U.S. patent application Ser. No. 12/534,857, filed on Aug. 4, 2009, which claims priority from U.S. Provisional Application 61/086,801, filed on Aug. 7, 2008, all of which are herein incorporated by reference in their entirety for all purposes.

BACKGROUND OF THE INVENTION

The present invention generally relates to processing of materials for growth of crystals. More particularly, the present invention provides a method for obtaining a gallium-containing nitride crystal by an ammonobasic technique, but there can be others. In other embodiments, the present invention provides an apparatus for large scale processing of nitride crystals, but it would be recognized that other crystals and materials can also be processed. Such crystals and materials include, but are not limited to, GaN, AlN, InN, InGaN, AlGaN, and AlInGaN, and others for manufacture of bulk or patterned substrates. Such bulk or patterned substrates can be used for a variety of applications including optoelectronic devices, lasers, light emitting diodes, solar cells, photoelectrochemical water splitting and hydrogen generation, photodetectors, integrated circuits, and transistors, among other devices.

Gallium nitride containing crystalline materials serve as a starting point for manufacture of conventional optoelectronic devices, such as blue light emitting diodes and lasers. Such optoelectronic devices have been commonly manufactured on sapphire or silicon carbide substrates that differ from the deposited nitride layers. In the conventional Metallo-Organic Chemical Vapor Deposition (MOCVD) method, deposition of GaN is performed from ammonia and organometallic compounds in the gas phase. Although successful, conventional growth rates achieved make it difficult provide a bulk layer of GaN material. Additionally, dislocation densities are also high and lead to poorer optoelectronic device performance.

Other techniques have been proposed for obtaining bulk monocrystalline gallium nitride. Such techniques include use of epitaxial deposition employing halides and hydrides in a vapor phase and is called Hydride Vapor Phase Epitaxy (HVPE) ["Growth and characterization of freestanding GaN substrates," K. Motoki et al., Journal of Crystal Growth 237-239, 912 (2002)]. Unfortunately, drawbacks exist with HVPE techniques. In some cases, the quality of the bulk monocrystalline gallium nitride is not generally sufficient for high quality laser diodes because of issues with dislocation density, stress, and the like.

Techniques using supercritical ammonia have been proposed. Peters has described the ammonothermal synthesis of aluminum nitride [J. Cryst. Growth 104, 411-418 (1990)]. R. Dwiliński et al. have shown, in particular, that it is possible to obtain a fine-crystalline gallium nitride by a synthesis from gallium and ammonia, provided that the latter contains alkali metal amides (KNH_2 or $LiNH_2$). These and other techniques have been described in "AMMONO method of BN, AlN, and GaN synthesis and crystal growth", Proc. EGW-3, Warsaw, Jun. 22 24, 1998, MRS Internet Journal of Nitride Semiconductor Research, http://nsr.mij.mrs.org/3/25, "Crystal growth of gallium nitride in supercritical ammonia" J. W. Kolis et al., J. Cryst. Growth 222, 431-434 (2001), and Mat. Res. Soc. Symp. Proc. Vol. 495, 367-372 (1998) by J. W. Kolis et al. However, using these supercritical ammonia processes, no wide scale production of bulk monocrystalline was achieved.

Dwiliński, in U.S. Pat. No. 7,160,388, which is hereby incorporated by reference in its entirety, generally describes an autoclave apparatus and methods for ammonothermal crystal growth of GaN. These conventional autoclave methods are useful for growth of relatively small GaN crystals but have limitations for large scale manufacturing. For example, apparatus with an inner diameter of 40 mm is somewhat useful for growing 1" diameter GaN crystals but is generally not suitable for larger scale growth of crystals. Evacuation of a conventional container, followed by chilling and flowing in gaseous ammonia, is for removing contaminants and filling with solvent at smaller reactor volumes, but may become problematic for large scale manufacturing. Although somewhat successful, drawbacks exist with these conventional ammonothermal techniques.

From the above, it is seen that improved techniques for crystal growth are highly desired.

BRIEF SUMMARY OF THE INVENTION

According to the present invention, techniques related to processing of materials for growth of crystal are provided. More particularly, the present invention provides a method for obtaining a gallium-containing nitride crystal by an ammonobasic technique, but there can be others. In other embodiments, the present invention provides an apparatus for large scale processing of nitride crystals, but it would be recognized that other crystals and materials can also be processed. Such crystals and materials include, but are not limited to, GaN, AlN, InN, InGaN, AlGaN, and AlInGaN, and others for manufacture of bulk or patterned substrates. Such bulk or patterned substrates can be used for a variety of applications including optoelectronic devices, lasers, light emitting diodes, solar cells, photoelectrochemical water splitting and hydrogen generation, photodetectors, integrated circuits, and transistors, among other devices.

In a specific embodiment, the present invention provides a bake/purge autoclave apparatus, fill with liquid NH_3, bleed off using H_2 gas with palladium (Pd) membrane. Additionally, the present invention provides a large scale high pressure ammonothermal apparatus, including seed rack, raw material basket, and baffle. Alternatively, the present invention provides a method of using an apparatus including: purging, baking during purging or evacuation, addition of liquid solvent (e.g., ammonia), removal of ammonia, recycling of ammonia, among other possible process steps.

In a specific embodiment, the present invention provides a process for growing a crystalline gallium-containing nitride. The process includes providing an autoclave comprising gallium-containing feedstock in one zone and at least one seed in another zone. The process also includes introducing a solvent capable of forming a supercritical fluid into at least the one zone and the other zone. In a preferred embodiment, the process maintains a pressure at or above about seven (7) atmospheres within the one zone and the other zone during introduction of the solvent into the one zone and the other zone. In a specific embodiment, the process includes processing one or more portions of the gallium-containing feedstock in the supercritical fluid to provide a supercritical solution comprising at least gallium containing species at a first temperature and growing crystalline gallium-containing nitride material from the supercritical solution on the seed at a sec-